CLAIMS:

1. Material for wear, erosion and corrosion resistant coatings, consisting of tungsten carbide alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.

2. Material in accordance with claim 1, wherein the said material is tungsten monocarbide WC alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.

3. Material in accordance with claim 1, wherein the said material is tungsten semicarbide W_2C alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.

4. Material in accordance with claim 1, wherein the said material is tungsten subcarbide W_3C alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.

5. Material in accordance with claim 1, wherein the said material is tungsten subcarbide $W_{12}C$ alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt%.

6. Material in accordance with claim 1, wherein the said material additionally contains fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

7. Material for wear, erosion and corrosion resistant coatings comprising a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

8. Coating, *characterised* in that it contains:

- an internal layer consisting of tungsten deposited on a substrate;
- and an external layer deposited on the said internal layer and containing tungsten carbide in accordance with claims 1-6.

9. Coating in accordance with claim 6, *characterised* in that its outer layer additionally contains a mixture of tungsten carbides in accordance with claim 7.

10. Coating in accordance with claims 8 or 9, *characterised* in that its outer layer additionally contains tungsten.

11. Coating in accordance with claims 8 or 9, *characterised* in that its outer layer additionally contains carbon.

12. Coating in accordance with any of claims 8 to 11, *characterised* in that its internal layer has a thickness of 0.5-300 μm and its outer layer has a thickness of 0.5-300 μm, with the ratio of thicknesses of the internal and external layers ranging from 1:1 to 1:600.

13. Process for producing tungsten carbides by chemical vapour deposition on a heated substrate using a mixture of gases including tungsten hexafluoride, hydrogen, a carbon-containing gas and, optionally, an inert gas, *characterised* in that the carbon-containing gas is thermally activated beforehand by heating to temperature 500-850°C.

14. Process in accordance with claim 13, *characterised* in that the said carbon-containing gas is propane.

15. Process in accordance with claims 13 or 14, *characterised* in that it is performed at a pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

16. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 1.0-1.5 and ratio of tungsten hexafluoride

to hydrogen 0.08-0.10, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, tungsten monocarbide WC is obtained.

17. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.75-0.90 and ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated beforehand to temperature 600-750°C; in this case, tungsten semicarbide W_2C is obtained.

18. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.05-0.55, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, tungsten subcarbide W_3C is obtained.

19. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.45 and ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, tungsten subcarbide $W_{12}C$ is obtained.

20. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.90-1.00 and ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, a mixture of the carbides WC and W_2C is obtained.

21. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.75 and ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated

beforehand to temperature 580-730°C; in this case, a mixture of the carbides W_2C and W_3C is obtained.

22. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, a mixture of the carbides W_2C and $W_{12}C$ is obtained.

23. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.45-0.60 and ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, a mixture of the carbides W_3C and $W_{12}C$ is obtained.

24. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.65-0.70 and ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, a mixture of the carbides W_2C, W_3C and $W_{12}C$ is obtained.

25. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, a mixture of the carbide WC and tungsten is obtained.

26. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.70-0.90 and ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated

beforehand to temperature 600-720°C; in this case, a mixture of the carbides W_2C and tungsten is obtained.

27. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.60-0.65 and ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, a mixture of the carbide W_3C and tungsten is obtained.

28. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.20-0.35 and ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbide $W_{12}C$ and tungsten is obtained.

29. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 0.35-0.60 and ratio of tungsten hexafluoride to hydrogen 0.05-0.07, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, a mixture of the carbides W_3C, $W_{12}C$ and tungsten is obtained.

30. Process in accordance with claim 15, *characterised* in that it is performed at a ratio of carbon-containing gas to hydrogen 1.50-1.70 and ratio of tungsten hexafluoride to hydrogen 0.10-0.12, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, a mixture of the carbide WC and carbon is obtained.

31. Process for the deposition of coatings consisting of an internal layer of tungsten and an external layer containing tungsten subcarbide $W_{12}C$ on substrates, preferably on construction materials and on items made from them, *characterised* in that the said process includes the following stages:

(a) placing the substrate in a chemical vapour deposition reactor;

(b) evacuating the reactor;

(c) heating the said substrate;

(d) supplying tungsten hexafluoride and hydrogen to the reactor;

(e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;

(f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;

(g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbides and mixtures of them with each other, with tungsten or with free carbon.

32. Process in accordance with claim 31, *characterised* in that it is performed at a reactor pressure of 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

33. Process in accordance with claim 31, *characterised* in that, before the application of a coating to materials or items made from materials selected from a group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical precipitation from aqueous solutions, electrolysis of melts or physical and chemical vapour precipitation.

34. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 1.00-1.50 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.10, and that the carbon-containing gas is heated beforehand to temperature 750-850°C; in this case, an external layer containing tungsten monocarbide WC is obtained.

35. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.75-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.06-0.08, and that the carbon-containing gas is heated beforehand to temperature 600-750°C; in this case, an external layer containing tungsten semicarbide W_2C is obtained.

36. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.050-0.055, and that the carbon-containing gas is heated beforehand to temperature 560-720°C; in this case, an external layer containing tungsten subcarbide W_3C is obtained.

37. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.35-0.40 and a ratio of tungsten hexafluoride to hydrogen 0.040-0.045, and that the carbon-containing gas is heated beforehand to temperature 500-700°C; in this case, an external layer containing tungsten monocarbide $W_{12}C$ is obtained.

38. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.90-1.00 and a ratio of tungsten hexafluoride to hydrogen 0.07-0.09, and that the carbon-containing gas is heated beforehand to temperature 670-790°C; in this case, an external layer containing a mixture of the carbides WC and W_2C is obtained.

39. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.75 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.060, and that the carbon-containing gas is heated beforehand to temperature 580-730°C; in this case, an external layer containing a mixture of the carbides W_2C and W_3C is obtained.

40. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.65-0.70 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-710°C; in this case, an external layer containing a mixture of the carbides W_2C, W_3C and $W_{12}C$ is obtained.

41. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.060, and that the carbon-containing gas is heated beforehand to temperature 570-700°C; in this case, an external layer containing a mixture of the carbides W_2C and $W_{12}C$ is obtained.

42. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.40-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.050, and that the carbon-containing gas is heated beforehand to temperature 550-680°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ is obtained.

43. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide W_2C and tungsten is obtained.

44. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.60-0.65 and a ratio of tungsten hexafluoride to hydrogen 0.055-0.070, and that the carbon-containing gas is heated beforehand to temperature 560-700°C; in this case, an external layer containing a mixture of the carbide W_3C and tungsten is obtained.

45. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.35-0.60 and a ratio of tungsten hexafluoride to hydrogen 0.050-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-690°C; in this case, an external layer containing a mixture of the carbides W_3C and $W_{12}C$ with tungsten is obtained.

46. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.20-0.35 and a ratio of tungsten hexafluoride to hydrogen 0.045-0.070, and that the carbon-containing gas is heated beforehand to temperature 500-680°C; in this case, an external layer containing a mixture of the carbide $W_{12}C$ and tungsten is obtained.

47. Process in accordance with claim 32, *characterised* in that it is performed at a ratio of the carbon-containing gas to hydrogen 0.70-0.90 and a ratio of tungsten hexafluoride to hydrogen 0.08-0.09, and that the carbon-containing gas is heated beforehand to temperature 600-720°C; in this case, an external layer containing a mixture of the carbide WC and tungsten is obtained.

48. Process in accordance with any of claims 31 to 47, *characterised* in that the coatings are deposited onto frictional assemblies.

49. Process in accordance with any of claims 31 to 47, *characterised* in that the coatings are deposited onto forming tools used for processing materials by means of pressing.

50. Process in accordance with any of claims 31 to 47, *characterised* in that the coatings are deposited onto components and units of machines and mechanisms operating with compressed gases and liquids or other pneumatic or hydraulic systems.

51. Material comprising:

- a substrate made from construction material;

- a coating deposited on the said substrate, consisting of an internal tungsten layer and an external layer containing tungsten carbide alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

52. Material in accordance with claim 51, wherein the said tungsten carbide is monocarbide WC.

53. Material in accordance with claim 51, wherein the said tungsten carbide is semicarbide W_2C.

54. Material in accordance with claim 51, wherein the said tungsten carbide is subcarbide W_3C.

55. Material in accordance with claim 51, wherein the said tungsten carbide is subcarbide $W_{12}C$.

56. Material comprising:

- a substrate made from construction material;

- and a coating deposited on the said substrate, consisting of an internal tungsten layer and an external layer containing a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

57. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides WC and $W_{12}C$.

58. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and W_2C.

59. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides W_3C and $W_{12}C$.

60. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C and $W_{12}C$.

61. Material in accordance with claim 56, *characterised* in that the external layer of the said coating contains a mixture of the tungsten carbides W_2C, W_3C and $W_{12}C$.

62. Material in accordance with claims 52-61, *characterised* in that the external layer of the said coating additionally contains tungsten.

63. Material in accordance with claims 52-61, *characterised* in that the external layer of the said coating additionally contains carbon.

64. Material in accordance with claims 52 to 63, *characterised* in that the internal layer of the said coating has thickness 0.5-300 μm and the ratio of thicknesses of internal and external layers ranges from 1:1 to 1:600.

65. Material according to claims 52 to 64, *characterised* in that the said substrate layer adjacent to the coating contains alloys with nickel content exceeding 25 wt%, e.g. Invar, Nichrome, Monel.

66. Material obtained by the process described in any of claims 31 to 47.

67. Multilaminar coating made from alternating layers of tungsten and layers containing tungsten carbide in accordance with any of claims 1 to 6.

68. Multilaminar coating made from alternating layers of tungsten and layers containing tungsten carbide in accordance with claim 7.

69. Multilaminar coating in accordance with claims 67-68, *characterised* in that the thickness of its individual layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

70. Process for the deposition of multilaminar coatings on substrates, preferably on construction materials and items made from them, consisting of alternating layers of tungsten and layers containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten or with free carbon, said process to include the following stages:

(a) placing the substrate in a chemical vapour deposition reactor;

(b) evacuating the reactor;

(c) heating the said substrate;

(d) supplying tungsten hexafluoride and hydrogen to the reactor;

(e) retaining the substrate in the said gaseous medium for the time interval necessary for the formation of the tungsten layer on the substrate;

(f) in addition to the said tungsten hexafluoride and hydrogen, supplying a previously thermally activated carbon-containing gas to the reactor;

(g) retaining the substrate in the gaseous medium formed at stage (f) for the time necessary for the formation of the outer layer containing tungsten carbide or mixtures of tungsten carbides with each other, with tungsten and with free carbon; stages (d) to (g) are repeated several times in order to form alternating layers of tungsten and layers containing tungsten carbides.

71. Process in accordance with claim 70, *characterised* in that it is conducted at reactor pressure 2-150 kPa, substrate temperature 400-900°C, ratio of carbon-containing gas to hydrogen 0.2-1.7 and ratio of tungsten hexafluoride to hydrogen 0.02-0.12.

72. Process in accordance with claim 70, *characterised* in that, before the application of a coating to materials or items made from materials selected from a

group including iron, carbon steels, stainless steels, cast irons, titanium alloys and hard alloys containing titanium, a coating is applied to them consisting of materials which are chemically resistant to hydrogen fluoride, namely nickel, cobalt, copper, silver, gold, platinum, iridium, tantalum, molybdenum and alloys, compounds and mixtures of these, by electrochemical or chemical precipitation from aqueous solutions, electrolysis of melts or physical and chemical vapour precipitation.

73. Process in accordance with any of claims 70 to 72, *characterised* in that the coating is deposited onto friction assemblies.

74. Process in accordance with any of claims 70 to 72, *characterised* in that the coating is deposited onto a forming tool used for processing materials by means of pressing.

75. Process in accordance with any of claims 70 to 72, *characterised* in that the coating is deposited onto units of machines and mechanisms operating with compressed gases and liquids or of other pneumatic or hydraulic systems.

76. Construction material comprising a substrate and a multilaminar coating consisting of alternating layers of tungsten and layers containing tungsten carbide alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluorine content up to 0.5 wt%.

77. Material in accordance with claim 76, wherein the said tungsten carbide is tungsten monocarbide WC.

78. Material in accordance with claim 76, wherein the said tungsten carbide is tungsten semicarbide W_2C.

79. Material in accordance with claim 76, wherein the said tungsten carbide is tungsten subcarbide W_3C.

80. Material in accordance with claim 76, wherein the said tungsten carbide is tungsten subcarbide $W_{12}C$.

81. Construction material comprising a substrate and a multilaminar coating consisting of alternating layers of tungsten and layers containing a mixture of at least two tungsten carbides alloyed with fluorine in amounts ranging from 0.0005 to 0.5 wt% and possibly with fluorocarbon compositions with carbon content up to 15 wt% and fluoride content up to 0.5 wt%.

82. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides WC and W_2C.

83. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides W_2C and W_3C.

84. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides W_3C and $W_{12}C$.

85. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides W_2C and $W_{12}C$.

86. Material in accordance with claim 81, wherein the said carbide layers contain a mixture of tungsten carbides W_2C, W_3C and $W_{12}C$.

87. Material in accordance with any of claims 76 to 86, *characterised* in that the said carbide layers additionally contain tungsten.

88. Material in accordance with any of claims 76 to 86, *characterised* in that the said carbide layers additionally contain carbon.

89. Materials according to any of claims 76 t0 88, *characterised* in that the thickness of its layers ranges from 2 to 10 μm and the ratio of the thicknesses of the alternating layers ranges from 1:1 to 1:5.

90. Construction material obtained by any of the processes described in claims 70 to 72.